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Kinetics of dehydrogenation of riebeckite $Na_2Fe^{3+}_2Fe^{2+}_3Si_8O_{22}(OH)_2$: An HT-FTIR study

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ABSTRACT

In this work, we address the kinetics of dehydrogenation occurring at high temperatures (HT) in riebeckite, a sodic amphibole with the ideal composition $Na_2Fe^{3+}_2Fe^{2+}_3Si_8O_{22}(OH)_2$. We performed isothermal experiments on both powders and single-crystals up to 560 °C and monitored the O-H stretching signal by Fourier transform infrared (FTIR) spectroscopy. Single-crystals show an initial increase in IR absorption intensity due to increasing vibrational amplitudes of the O-H bond stretching, not observed for powders. The OH-intensities vs. time were fitted using the formalism for first-order reactions. The calculated activation energies for H^+ diffusion in riebeckite are 159 ± 15 kJ/mol for powders and 216 ± 20 kJ/mol for single crystals, respectively. The exponential factor m in the Avrami-Erofeev equation obtained for crystals ranges between 1.02 and 1.31, suggesting that, unlike powders, the dehydration process in crystals is not a purely first-order reaction. This implies that a second energy barrier must be considered, i.e., diffusion of H^+ through the crystal. FTIR imaging showed that H^+ diffusion occurs mainly perpendicular to the silicate double-chain. Our results confirm that the release of H^+ from riebeckite occurs after the irreversible Fe^{2+}-to-Fe^{3+} exchange, thus at temperatures >550 °C. To be effective, the process needs the presence of external oxygen that, by interacting with H^+ at the crystal surface, triggers the release of H_2O molecules. This implies that oxidizing conditions are required for the amphibole to be an efficient water source at depth.

Keywords: Riebeckite, HT-FTIR spectroscopy, FTIR imaging, Fe-oxidation, dehydration kinetics, activation energy